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to a certain sub-class [X], of [H]. If the forms of [H] are not all generic from this new point of view, we may adopt a new canonical form for the exceptional ones, and continue in this way.

We have observed that the coefficients of a unique canonical form are absolute invariants, and moreover one-valued invariants, in the sense, that their values are uniquely determined as soon as the coefficients of the form F are given. In the ordinary theory of algebraic invariants, it is at once apparent that these invariants are algebraic functions of the coefficients of F. Consequently it follows from their one-valuedness that, in this case, these invariants are *rational* functions of the coefficients. In the theory of invariants of linear differential equations, the uniquenes of a canonical form gives rise to invariants which are rational functions of the coefficients of the differential equation and of their derivatives.

There are many cases in which a k-valued canonical form is obtained rather than a unique one. That is, if we resume our terminology, the sub-class [Φ] contains not merely one, but exactly k forms $\Phi_1, \Phi_2, \ldots, \Phi_k$, each of which is equivalent to F by a transformation of the group G. *The coefficients of these canonical forms will still be absolute invariants of F, but they will be k-valued functions of its coefficients.* It is obviously possible to find an equation of degree k with one-valued invariants as coefficients, of which these k-valued invariants are the roots. In the theory of algebraic invariants we obtain in this way irrational invariants, as roots of an equation whose coefficients are rational invariants.

TYPES OF PHOSPHORESCENCE

By Edward L. Nichols and H. L. Howes

Department of Physics, Cornell University

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The existence of phosphorescence of exceedingly short duration was long ago revealed by the phosphoroscope of Becquerel but, until very recently the afterglow of luminescent bodies has been studied quantitatively, only where it is of comparatively long duration. Curves of decay were supposed to be all of the same character. It was assumed that the law of diminution of brightness, as expressed by the equation

$$I = \frac{1}{(a_1 + b_1 t)^2} + \frac{1}{(a_2 + b_2 t)^2}$$

was of general application and that the phosphorescence of various substances differed only in color, brightness and duration.

The measurements of Waggoner[1] and of Zeller[2] on phosphorescence of short duration tended to confirm this view. On the other hand the observations of

Ives and Luckiesh[3] on the effect of temperature upon the curves of decay of certain phosphorescent sulphides might seem to demand a modification of the usual law in certain cases, while the studies of the phosphorescence of gases by C. C. Trowbridge[4] and of paraffine at liquid air temperatures by Kennard[5] indicate that for the range covered by their measurements the law of decay cannot be expressed by a summation of $1/(a + bt)^2$ terms.

In a recent investigation[6] we have found the exceedingly brief phosphorescence of the uranyl salts, which, although very brilliant lasts only for about 0.03 seconds, to be of an entirely different type. It decays very slowly at first and later very rapidly, whereas in all cases previously studied the opposite is true. Measurements just completed on the luminescence of calcite indicate that this newly determined form of decay curve is not confined to the uranyl salts.

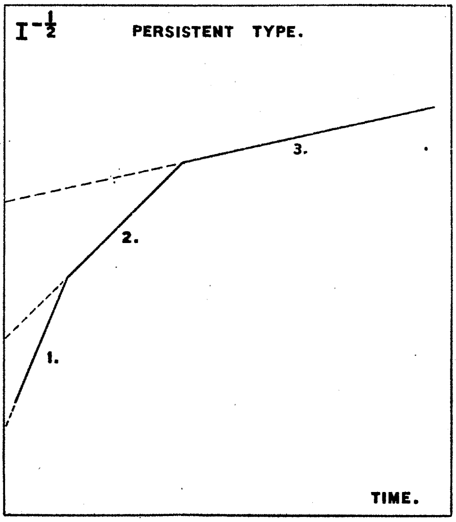

FIG. 1

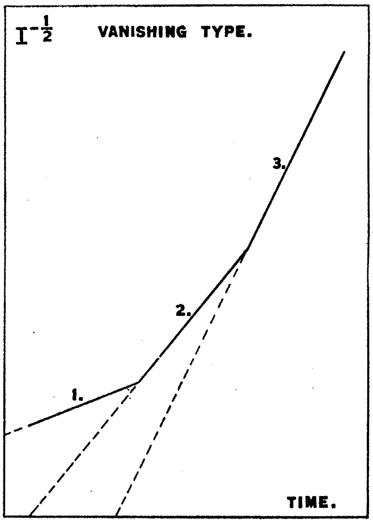

FIG. 2

We propose therefore to recognize two distinct types of phosphorescence and to designate them as *persistent phosphorescence* and *vanishing phosphorescence.* They are sharply distinguished from one another by the following characteristics.

Types of phosphorescence.—1: (Characteristic of persistent phosphorescence.) This type has a curve of decay made up of a succession of linear process, of diminishing slope as we proceed from the origin of time (fig. 1). Three or more such processes have been found in all cases which have been studied through a sufficient range.

2: (Characteristic of vanishing phosphorescence.) This type has a curve of decay made up of a succession of linear processes, of increasing slope as we proceed from the origin of time (fig. 2).

It is understood that in these specifications and elsewhere, unless otherwise stated, the curve of decay is plotted with time from the close of excitation as abscissae and the reciprocal of the square root of intensity ($I^{-\frac{1}{2}}$) as ordinates. A linear process is any straight portion of the graph; as *1*, *2* or *3* in figures 1 and 2. The inference is that the more or less abrupt changes of slope are related to and indicative of real changes in the *processes* by which the emission of light from the phosphorescing body is being maintained.

A distinguishing criterion of type is found in the sign of the intercepts of the various processes at the origin of time. In type 1 the intercepts are all positive; in type 2 the intercepts of process 2 and 3 are negative.

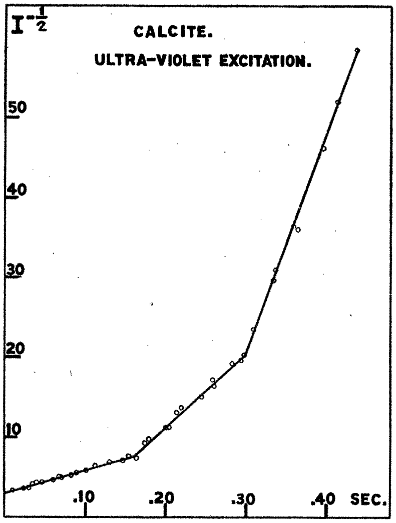

FIG. 3

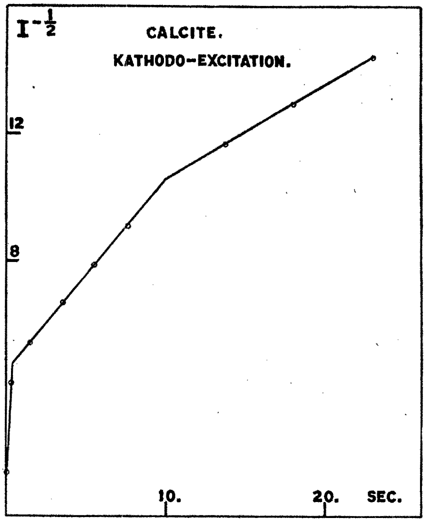

FIG. 4

The passage from one process to the next is presumably never actually discontinuous, as in the above diagrams, but it is sometimes very abrupt as in the curves of figures 3 and 4 which are from our recent measurements of the phosphorescence of calcite. Sometimes the transition from slope to slope is very gradual; so that the first and second processes tend to merge into a curved line. We have shown,[6] in the case of the uranyl salts that the location of the knees depends on the intensity of the excitation and that distributed knees —so to speak—occur when the exciting light penetrates the crystal and being absorbed produces luminescence of decreasing intensity in successive layers; also that where the conditions are such that excitation is confined chiefly to the surface, the knees are well defined.

Similar modifications of the curve occur in kathodo-excitation, and distributed knees are then probably due to a kathodic discharge containing particles of varying velocity.

Both types may occur in a single substance.—Shortly after the completion of our experiments on the vanishing phosphorescence of the uranyl compounds, Misses Wick and McDowell[7] found that some of the same salts, notably $K.UO_2(NO_3)_3$ and $K_2UO_2(NO_3)_4$ when exposed to the kathode discharge at the temperature of liquid air glowed for many seconds after the close of excitation with decay curves of the persistent type. At + 20° the effect is either absent or excessively feeble. Not all the uranyl salts, even among those that are reasonably stable in vacuo, respond to the action of the kathode discharge to a measureable extent.

The Franklin Furnace calcites, as we discovered in our recent investigation,[8] have the same remarkable property, i.e., vanishing phosphorescence under photo-excitation and persistent phosphorescence under the kathode discharge. Figures 3 and 4 exhibit the vastly different behavior of the same calcite after the close of these two modes of excitation.

Both types of phosphorescence are obtainable with calcite at any temperature between $-180°$ and $+300°$.

Independence of the two types.—Since the kathode discharge modifies the surface layers of substances subjected to its action, it might be supposed that calcite crystals after kathodo-bombardment would show persistent phosphorescence when photo-excited. To test this supposition we placed a crystal of the Franklin Furnace calcite in the bottom of a V shaped vacuum tube having a quartz window.

It could thus be excited either by the kathode discharge or from an iron spark. Previous excitation by the kathode rays had no observable effect on the photo-phosphorescence which was of the vanishing type and had approximately at least the normal color, brightness and duration. The photo-phosphorescence could be superimposed upon the persistent kathodo-luminescence, as a fleeting effect, at any time during the life of the latter either after or before the close of the kathodo-excitation. Apparently the two were entirely independent of each other.

Misses Wick and McDowell had previously made a similar observation in their study of the kathodo-phosphorescence of the uranyl salts; i.e. that the kathode rays do not render them capable of persistent photo-phosphorescence.

Apparent occurrence of both types with a single source of excitation.—Willemite is one of the most brlliant of luminescent substances. The afterglow is commonly fleeting, but masses are occasionally found which exhibit phosphorescence of long duration. Such specimens are persistent under photo-excitation and kathodo-excitation alike. The phosphorescence of the other variety, unlike that of calcite and of the uranyl salts, is of short duration under both kinds of excitation.

The determination of the decay of phosphorescence of a specimen of the latter variety, using the disk phosphoroscope, gave curves like that plotted in figure 5. Processes 1 and 2 are of type 1 (vanishing) but these are followed by a process 3 of lesser slope.

This is obviously a composite curve due to the superposition of phosphorescence of both types. It does not follow however that it is a true example of a *single substance* brought to both types of phosphorescence by photo-excitation. The evidence is to the contrary.

1. The two varieties of willemite are commonly associated. One of our specimens contains parallel veins of the persistent form and of willemite of short duration in the same matrix.

2. Willemite is associated with the Franklin Furnace calcite.

That the vanishing phosphorescence in the curve in figure 5 may be due to an admixture of calcite is suggested by the following observations.

a. When the disk of the phosphoroscope, coated with the powdered willemite and exposed to the light of the iron spark, was driven rapidly, the region nearest the spark in the direction of revolution but shielded from the direct light was a brilliant yellow-green, the regions approaching the spark but shielded, were of a dark *blue*-green. This is the effect which would be expected were calcite present, since its red-yellow phosphorescence would give the yellowish caste during the first process of decay but would vanish before the revolution of the disk was completed.

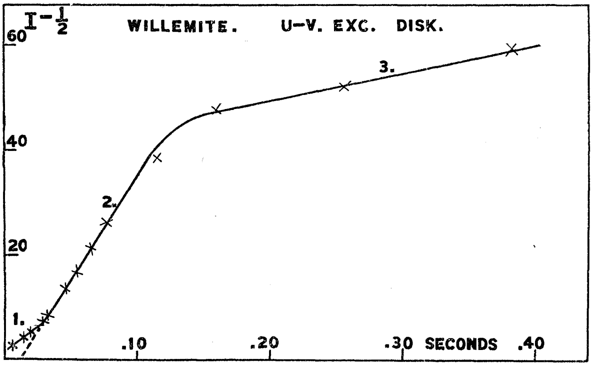

FIG. 5

b. When the collimator of a spectroscope was directed to the rapidly revolving disk the spectrum of the phosphorescent willemite appeared as a broad continuous band extending from the extreme red to the blue. The crest was approximately at 0.54 μ and there was suspicion of a weak region in the yellow.

At a somewhat lower speed, which allowed a longer interval of time between excitation and observation the red end of the spectrum disappeared and at a much lower speed the yellow and brightest part of the green vanished leaving a much narrower band in what had been a comparatively feeble region, with its crest in the blue green at about 0.52 μ.

The former brilliant crest at 0.54 μ was now very dim and lay near the edge of the persistent band. This persistent crest coincides in position with that of the fluorescence spectrum of a willemite of long duration determined spectrophotometrically some years ago.[9]

Obviously we have in this spectrum two, and perhaps three overlapping bands. A very rapid red band, presumably due to calcite, the band of the willemite of short duration and a persistent band of small intensity indicative of the presence of willemite of long duration.

Not all specimens of willemite have the complicated curve of decay above described. Waggoner,[1] (1908) in his studies of phosphorescence of short duration, determined the beginnings of the curves of decay of two willemites; one of the rapid and one of the persistent variety. He used the Merritt phosphoroscope having a range up to 0.06 seconds. His curves are of the persistent type.

Not all phosphorescence of quick decay is of the vanishing type.—That the type of phosphorescence is not altogether a question of duration we have abundant evidence. The willemite of quick decay measured by Waggoner is of much shorter measurable duration than the Franklin Furnace calcites, yet its curve of decay is clearly of the opposite type. The same is true of various phosphorescent compounds prepared by Waggoner, i.e., $ZnCl_2$, CdCl, $CdSO_4$,—each with a trace of $MnSO_4$ added, which were heated to redness with a flux of Na_2SO_4. Although their phosphorescence is of brief duration they gave decay curves of the persistent type.

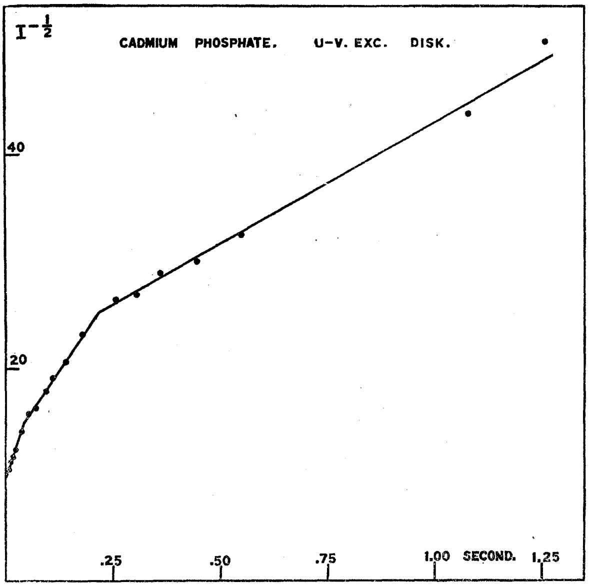

FIG. 6

There is this distinction between the luminescence of such substance and vanishing phosphorescence. The latter becomes completely extinct almost immediately after it ceases to be of measurable intensity; as indicated by the steepness of the second and third processes (fig. 2). In the persistent type of short duration the loss of light during the initial process may go to the very limit of visibility within a few hundredths of a second or less, but if the threshold is not actually crossed the phosphorescence may remain, barely visible in a completely dark room, for a considerable time. Waggoner remarks (on page 216 of his paper) "*It will be noted that in practically all the substances studied, the measurable portion of the decay is over in 0.07 seconds. Some of the substances may, however, be seen in a dark room for a very much longer time.*"

Phosphorescence of short duration, when *not* of the vanishing type, may be considered simply as a case of the persistent type in which the rapid initial process reduces the intensity nearly to or beyond the threshold of visibility. The subsequent processes, though gradual are therefore too faint for observation or invisible. The brightness of the first process may be as great or greater in cases of quick decay than where the phosphorescence continues of measurable intensity for a long time. Zeller[2], who has studied the beginnings of decay of the phosphorescence of various persistent compounds has made note of the fact that duration is not in any simple way related to initial brightness. In a group of phosphorescent cadmium compounds, in particular, some that were too dim for measurement with the phosphoroscope remained visible for a long time while those of greatest initial intensity were of very short duration.

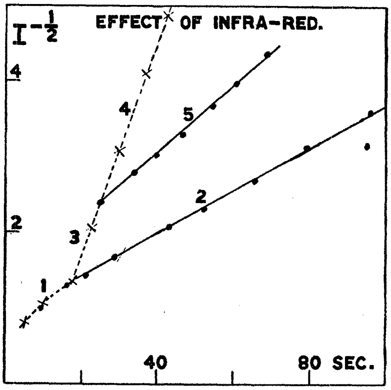

FIG. 7

An interesting substance which came to our notice during these investigations through the kindness of Mr. W. L. Lemcke is a cadmium phosphate prepared by Mr. W. S. Andrews. Under the iron spark it is excited to a fine white phosphorescence having a measurable duration of about one second. We determined its curve of decay with the disk phosphoroscope. As may be seen from figure 6 it is of the persistent type and so far as the white afterglow is concerned might be classed as of rather short duration; but a very faint ruddy phosphorescence remains for a much longer time. This specimen, as viewed on the rotating disk is remarkable for the succession of color effects which it exhibits. Pink, very fleeting, is followed by nearly pure white, then for an instant by blue which goes over into a very persistent pink, turning ruddy as decay progresses.

Such color changes in other substances have been shown to be due to the existence in the phosphorescence spectrum of overlapping bands having different rates of decay and the striking display would seem to indicate an unusual complexity of composition. We were surprised, therefore, to learn from Mr. Andrews that for the production of this brilliant white phosphorescence cadmium phosphate of exceptional purity is necessary, and that there is no admixture of other metallic salts, as in the preparation of the phosphorescent sulphides.

Curves exhibiting the new vanishing type of decay, above described, resemble nothing in the earlier work on phosphorescence so much as the curves obtained as a result of the action of infra-red light on Sidot Blende.[1] Figure 7 exhibits this phenomenon. Processes 1 and 2 together show the pure decay curve, without infra-red, but if the infra-red is applied after 18 seconds of decay the more rapid process 3–4 ensues. If, however, the infra-red is removed at the end of 25 seconds the decay resumes a slower rate, as shown by process 5. Processes 1, 3 and 4 taken together show a striking resemblance to the vanishing type of decay. Attempts to hasten the decay of calcite or of the phosphorescent uranyl salts by infra-red action however have yielded no result. Here the successively steeper processes must be due to a change in the rate of recombination of the ejected electrons with the active phosphorescing groups. It is commonly believed that only certain groups of particles are active, the majority being considered to be inactive. It is evident that these changes in rate of decay are inherent with the crystal and must be due to a more or less sudden change in the internal conditions. The electric fields within a crystal are so strong that it is perhaps not surprising that the infra-red field, applied from the outside, cannot affect either the phosphorescent action in the active groups or increase the number of free electrons. The sudden change in the rate of decay may be due to a change in the electric field concomitant with the changed orientation of the charged particles, which drives the ejected electrons in greater proportion to the non-active parts of the molecule.

[1] Waggoner, *Physic. Rev., Ithaca,* (Ser. 1), **27**, 1908, (209).

[2] Zeller, *Ibid.*, **31**, 1910, (367).

[3] Ives and Luckiesh, *Astroph. J., Chicago,* **36**, 1912, (330).

[4] Trowbridge, C. C., *Physic. Rev.*, **32**, 1911, (129).

[5] Kennard, *Ibid.*, (Ser. 2), **4**, 1914, (278).

[6] Nichols and Howes, *Ibid.*, **9**, 1917, (292).

[7] Wick and McDowell, *Ibid.*, **11**, 1918, (421).

[8] To be described in a forthcoming number of the *Physical Review.*

[9] Nichols and Merritt, *Ibid.*, (Ser. 1), **28**, 1909, (349).

[10] Nichols and Merritt, *Studies in Luminescence, Carnegie Inst., Washington, Pub.*. 152, 1912.